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TRIALS ON SYNTHESIS OF SYNTANS FROM VARIOUS MONOMERS AND DETERMINATION OF THEIR TANNING PERFORMANCES

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Abstract: *The present study report on the attempts of synthesis of synthetic tanning agents based on different starting materials of phenol, urea, salicylic acid, resorcinol, dihydroxydiphenyl sulfone via condensation with formaldehyde. After many trials, best results were obtained from phenol-formaldehyde, phenol-urea-formaldehyde and dihydroxydiphenyl sulfone-formaldehyde systems. It was shown that the experiments with other starting materials need further investigations and more detailed studies for controlled reactions to obtain usable resins. The pH values and dry matter contents of the successful resins obtained from reactions were determined and the structural analysis was done by FTIR. Then the produced syntans were used as solo tanning agents for the tanning of pickled sheep skins. The results showed that all the leathers tanned with the synthesized syntans had shrinkage temperatures over 70 °C. Moreover, the filling coefficients of the produced syntans, the physical properties of the leathers in terms of tensile strength, percentage of elongation and tear strength were investigated. The produced syntans gave very white and/or light beiege colors with a good filling effect and plain grain structure.*

Key words: *Leather, Tanning, Synthetic Tannin, Syntan, Resin*

1. INTRODUCTION

Tanning, which is the basic process of leather production, is one of the first production processes of human being [1]. Tanning can simply be defined as the process of converting the organic leather raw material, which is putrescible by bacterial activities, into an impurtescible and stable material [2]. Approximately 80-85% of the leathers produced in the world are tanned with basic chromium-sulphate compounds [3-4]. Chrome-tanned leathers are particularly characterized by their lightness and high tensile strength. This is due to the fact that chromium forms crosslinks between polypeptide chains by making coordination bonds with acidic amino acid side groups in skin collagen [5]. This cross-linking causes significant increases in the physical and mechanical properties of chrome-tanned leathers and can increase the wet thermal resistance of leathers up to 100 °C. Besides all these advantages of chrome, it also has some negative features. However, the main disadvantage of chrome tanning is generation of liquid and solid wastes containing chromium (a heavy metal that has negative effects on human health and the environment) at the end of the process, since the consumption of chrome tanning materials is 60-70% [5]. For these reasons, due to the increasing environmental pressure and the support given to environmental production in recent years, chrome tanning has become controversial. So, the studies on minimizing the use of chromium, increasing its consumption, recycling it or using alternative tanning agents have come to the fore. Demands for leather products such as chrome-free or metal-free have started to increase in the sector, and this has gradually increased the importance of alternative tanning agents. The production of metal-free leather, which has started to develop in the European market in recent years and is expected to increase worldwide in the coming years, has gained importance.

Considering the current technologies in the production of this type of leather, it is seen that aldehyde, vegetable tannins and syntans come to the fore as tanning agents. Among them, aldehydes are limited to use alone because they do not have a sufficient filling effect on the leather and may have harmful effects on human health. Vegetable tannins, on the other hand, have been used for many years, but they cannot be used for every leather type and are preferred for certain product groups, since they coarsen the grain, have low light fastness, and give leathers in light and dark brown color tones. However, syntans are increasing in use in the production of metal-free leathers, as they can be used as substitutes for vegetable tannins in a wider range of products, and because they provide leather with lighter color tones and relatively higher light fastness. Synthetic tannins or syntans have been used in the leather industry for many years [6-10]. The first phenolic syntan was obtained by Stiasny in 1911 by condensation of phenol with formaldehyde and sulfonation with sulfuric acid. In addition, the first comprehensive information on the production and use of synthetic tannins was reported by Wolesenksy and Stanley [11-15].

Due to the increasing environmental awareness in recent years, the importance of alternative tanning agents to chrome tanning materials, which are the most used tanning agents, is gradually increasing. For this reason, the use of both vegetable tanning and synthetic and polymeric tanning agents has increased and R&D studies in this field have been accelerated [16].

From this point of view, in our study many trials were carried out on the synthesis of synthetic tannins via condensation with formaldehyde, using different starting monomers such as phenol, urea, resorcinol, salicylic acid, dihydroxydiphenic sulfone. It is aimed to reveal the production of synthetic tannins containing different starting materials in detail and comparatively with an academic approach. In addition, synthesized syntans were used as solo tanning agents in tanning process, then their tanning performances and their effect on the leather properties were examined.

2. MATERIALS and METHODS

2.1 Materials

For the synthesis of syntans Phenol (Ph, TEKKİM, %85), Urea (Merck, %99), Salicylic acid (SA, Merck, %99), Resorcinol (Rc, Merck, %99), Dihydroxydiphenyl sulfone (DHDPS, Merck, %98) and Formaldehyde (FA, TEKKİM, %37) were used as different starting monomers. Sulfuric acid (TEKKİM, 95-98%) was used as catalyst and sulfonation agent in the reactions. The neutralization and pH adjustment of the syntan solutions was done by 1M NaOH (TEKKİM, 98%) solution. The polymerization reactions took place in 2 necked 250-1000 mL glass balloons equipped with a condenser. Heating and mixing procedures was done in glycerin bath by using a Heidolph magnetic stirrer. For tanning trials Metis type pickled sheep skins were used.

2.2. Methods

2.2.1 Syntheses of syntans

In the study many trials on the condensation of phenol, salicylic acid, recorsinol, phenol-urea, dihydroxydiphenyl sulfone with formaldehyde were performed. Table 1 shows the details of all polymerization reactions performed. For condensation, first novalac type reactions were performed (F1-F3). The water solubility of the final resins was found to be low, thus, all the other condensation trials were carried out using nerodol type reactions for all monomers.

In the trials mol ratios of the starting materials and reaction temperatures were varied. After all trials, salicylic acid-formadehyde and recorsinol-formaldehyde based condensation did not give any soluble final resins. For these trials further detailed investigations were found to be necessary. On the otherhand successful condensation reactions were obtained for phenol-formaldehyde, dihydroxydiphenyl sulfone-formaldehyde and phenol-urea-formaldehyde resins. From each group one resin gave the optimal results were re-produced in larger scale (Table 4) and used for the leather application as solo tanning agent.

As an example for the synthesis of syntans; 23,5 g phenol and 28,4 g H_2SO_4 were mixed at 90 °C over night for sulfonation. Next morning the system was cooled down, 5.6 g of water was added and 15,2g formaldehyde was dropped in the reaction for 90 min. Afterwards, the reaction temperature was raised to 75 °C and kept 3h for the completion of condensation. At the end the reaction the system was cooled down to room temperature and pH was adjusted between 5,0-6,0 with 1M NaOH solution. The final solutions were used directly in tanning process.

Table 1. *Polymerization trials on syntan synthesis using different starting monomers*

Code	Ph (mol)	SA (mol)	RS (mol)	DHDPS (mol)	Urea (mol)	H_2SO_4 (mol)	FA (mol)	Reax. Temp (°C)	Final Solid content (%)
F1	0,50	-	-	-	-	0,50	0,29	40	32
F2	0,50	-	-	-	-	0,24	0,29	40	30
F3	0,50	-	-	-	-	0,30	0,40	40	45
F4	0,10	-	-	-	-	0,10	0,08	70	49
F5	0,25	-	-	-	-	0,28	0,1375	35	44
F6	0,25	-	-	-	-	0,28	0,1375	40	39
F7	0,25	-	-	-	-	0,28	0,1875	40	52
F8	0,25	-	-	-	-	0,28	0,23	35	55
S1	-	0,250	-	-	-	0,002	0,1875	75	X
S2	-	0,0625	-	-	-	0,07	0,04687	70	14
S3	-	0,125	-	-	-	0,14	0,094	70	X
S4	-	0,125	-	-	-	X	0,094	80	X
R1	-	-	0,20	-	-	1 drop	0,1060	70	X
R2	-	-	0,25	-	-	0,14	0,1875	120	X
R3	-	-	0,25	-	-	0,28	0,1875	90	X
R4	-	-	0,25	-	-	0,20	0,1875	50	X
D1	-	-	-	0,25	-	0,28	0,1375	70	41
D2	-	-	-	0,25	-	0,28	0,1875	70	39
F-U1	0,50	-	-	-	0,45	0,50	0,50	70	X
F-U2	0,50	-	-	-	0,40	0,50	0,50	70	X
F-U3	0,50	-	-	-	0,33	0,50	0,50	70	43
F-U4	0,50	-	-	-	0,25	0,50	0,50	70	45

2.2.2. Tanning application

For the preparation to the tanning process the pickled sheep skins were first depickled followed by acidic sammying and degreasing procedures. The tanning procedure was given in Table

2. After tanning process, the leathers were rested for a week, shaved and then a conventional retanning/lubrication process was applied (Table 3). After the wet processes completed the leathers were dried, mill drummed and toogled.

Table 1. *The recipe where the produced syntans were used as solo tanning agent*

Process	Amount (%)	Chemical	Temperature (°C)	Duration (min.)	pH
Pickle&tanning	70	Water	30	10	-
	10*	Syntan	-	60	-
	1,5	Synthetic fatliquoring agent	-	30	-
	10*	Syntan	-	60	-
	5*	Syntan	-	60	-
Fixation	1	Formic acid	38	90	3.5
Washing	100	Water	25	5	-

*based on dry content of the syntan solution

Table 3. *The recipe of the retanning and fatliquoring process applied to tanned leathers*

Process	Amount* (%)	Chemical	Temperature (°C)	Duration (min.)	pH
Neutralization	200	Su	35	5	-
	2	Neutral syntan	35	60	4,5-5,0
Retanning	2	Amphoteric polymer	-	45	-
Fatliquoring	9	Combined fatliquoring agent	45	60	-
Fixation	1,5	Formic acid	-	120	3,8-4,0
Ø					
Washing	100	Water	25	10	-

*based on shaved weight

2.2.3 Characterization of synthesized resins

The structural characterization of the synthesized resins was carried out by FTIR spectroscopy using Perkin Elmer Spectrum-100 model FTIR-ATR spectrometer. For this purpose, dried samples were scanned within the range of 4500 – 600 cm^{-1}. Other physical properties of the resins such as pH (pH meter) and dry matter (gravimetrically) were also measured.

2.2.4 Determination of Physical Properties of the Leathers

After completing the tanning processes, the shrinkage temperatures of tanned leathers were determined according to standard method of IUP 16 [17]. Filling coefficiency of the leathers were determined by measuring the thickness of the leathers before and after tanning process. The physical properties such as tensile strength, percentage of elongation, tear strength were tested according to TS EN ISO 3376 and TS EN ISO 3377-2 standard test methods [18,19].

3. RESULTS and DISCUSSIONS

3.1 Synthesis of the syntans

As explained in the method section three selected syntans gave successful results were produced relatively in higher amount (300g). The resin types, molar ratios of the starting monomers, their final pH and solid content were given in Table 4. All the resins were obtained coagulum free, dark reddish-brown colored solutions.

Tablo 2. *The selected syntans synthesized in higher scale and their properties*

Syntan no	Content	Molar ratios	pH	Solid content (wt%)
1	Phenol-Formaldehyde (PF)	1 / 0,75	5,0	45
2	Phenol-Urea-Formaldehyde (PUF)	1 / 0,5 / 1	5,3	48
3	Dihydroxydiphenyl sulfone -Formaldehyde (DF)	1 / 0,75	5,6	42

3.2 FTIR analysis

Structural analysis of synthesized synthetic tannins was done by FTIR. The Spectra of large scale produced syntan samples are given in Figure 1 and detailed analysis of the spectra are given in Table 5. When the spectra of the synthetic tannin samples are examined, the –NH stretching vibration of urea-containing syntan is at 3375 cm^{-1}, the phenolic –OH absorption band was around 3280 cm^{-1} as a wide peak, the C=O and N–H bands of the urea groups were observed at 1723 cm^{-1}. Absorption peaks of aromatic C=C vibrational stretch belonging to phenol and dihydroxydiphenyl sulfone groups were observed at 1590 and 1431 cm^{-1}, aliphatic –CH stretching at 1501 and 1110 cm^{-1}, C-O stretching at 1645 cm^{-1}. The results show that synthetic tannins were successfully synthesized.

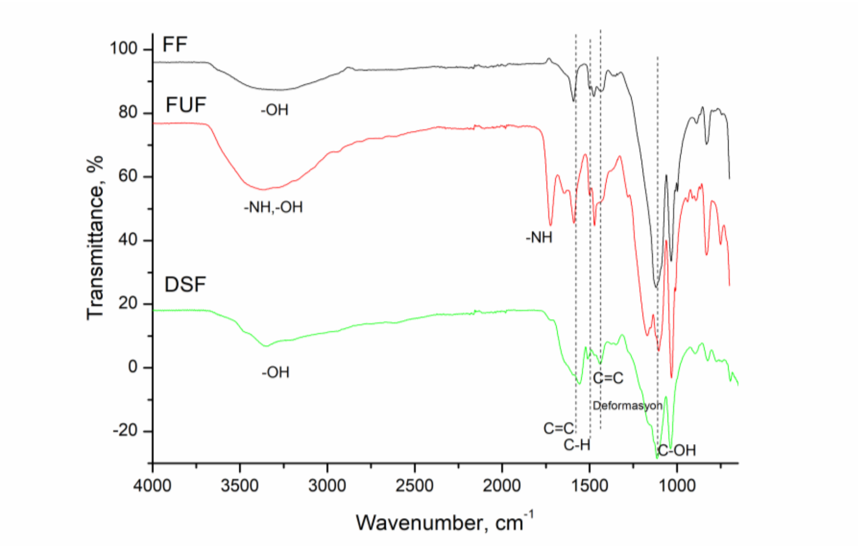

Fig. 1. *IR spectra of phenol, formaldehyde and synthesized phenolic syntan samples*

Table 3. *IR absorption bands of synthetic tannin samples and related absorption groups*

Wavenumber, (cm^{-1})	Relevant group absorption
3375	-NH stretching
3280	-OH stretching
1723	-C=O stretching
1645	-NH stretching
1590	C=C aromatic ring
1558	C=C aromatic ring
1431	C-H aliphatic
1432	C = C, CH_2- benzene ring veiled with methylene groups
1110	C-O stretching
1030	C-O stretching of -CH_2OH groups

3.3. Leather properties

The synthesized syntans were used successfully in the tanning process without any problems. It was observed that the consumption of syntans was very good at the end of tanning process. It was also observed that the leathers obtained were full-handed, light-colored and had smooth-grain. The leather images taken at the end of the tanning and after drying were shown in Figure 2.

In Table 6 the other leather properties obtained from physical tests were summarized. During the tanning process with synthetic tannins, it was observed that the bath was clean at the end of tanning process indicating that the consumption of the synthetic tannins by the leathers was high. As can be seen from the results given in the Table 6, an increase was observed in the average thickness of all leathers after tanning. The filling coefficiency of the syntans were found to be 21,41%, 25,40% and 42,74% for phenol-formaldehyde resins, phenol-urea-formaldehyde and dihydroxydiphenyl sulfone-based synthetic tannins, respectively. The results showed that the thickness of the leathers increased significantly after tanning, and the highest increase was obtained with dihydroxydiphenyl sulfone based synthetic tannins.

Fig. 2. *Leather images taken at the end of tanning process and after drying (From left to right: Leathers tanned with Phenol-FA, Phenol-Urea-Formaldehyde, Dihydroxydiphenylsulfone-Formaldehyde)*

The shrinkage temperature values of the leathers were shown also in Table 6. According to the results, the highest shrinkage temperature of 74 °C was observed for leathers tanned with phenol-formaldehyde resin. This was followed by dihydroxydiphenol sulfone at 72 °C and phenol-urea-formaldehyde resin at 70 °C. The results showed that all the synthesized syntans had good tanning ability.

When the mechanical properties were evaluated it was observed that highest values of tensile strength, elongation percentage and tear strength were in the order of dihydroxydiphenylsulfone-formaldehyde, phenol-urea-formaldehyde and phenol-formaldehyde, respectively.

Table 6. *Leather properties*

Reçine No	Filling coefficiency (%)	Shrinkage temperature (°C)	Tensile strength (N/mm^2)	Elongation percentage (%)	Tear strength (N/mm)
1	21,41	74	9,44	53,01	26,12
2	25,40	70	14,38	60,10	40,48
3	42,74	72	16,06	87,81	79,36

4. CONCLUSION

In the study, synthetic tannin syntheses were carried out, which includes the condensation reactions of different starting materials such as phenol, phenol-urea, resorcinol, salicylic acid and dihydroxydiphenyl sulfone with formaldehyde. Among these, successful results were obtained from phenol-formaldehyde, phenol-urea formaldehyde and dihydroxydiphenyl sulfon-formaldehyde-based samples. It has been observed that trials with other starting materials require further and detailed laboratory studies. However, resin production of phenol, phenol-urea, dihydroxydiphenyl sulfone with formaldehyde have been carried out successfully. The obtained resins were then used in the tanning process as solo tanning agents, and shrinkage temperatures of 70°C and above were obtained in all trials. It has been observed that leathers tanned with synthetic tannins gave leathers with white and light beige color tones with high fullness and smooth grain. It was also observed that phenol-formaldehyde resins had high tanning ability, but gave tighter and relatively low elasticity leathers, while the leathers tanned with dihydroxydiphenyl sulfone-formaldehyde resin had higher flexibility and fullness.

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5. REFERENCES

[1] M. Kite, and R. Thomson, "*Conservation of Leather and Related Materials*", UK:Elsevier, 2007.

[2] A. D. Covington, "*Tanning Chemistry, the Science of Leather*" Cambridge: The Royal Society of Chemistry Publishing, 2009.

[3] M.A. Eid, E.H.A. Nashy, E.A. El-Ashkar, K.A. Eid, E.H. Borai, "*Speciation of Chromium İons İn Tanning Effluents And Subsequent Determination Of Cr(VI)*", Journal of the American Leather Chemists Association, vol. 97, pp. 451, 2002.

[4] C. Hauber and H.P. Germann, "*Investigation On A Possible Formation And Avoidance Of Chromate İn Leather*", World Leather, October, pp. 73-80, 1999.

[5] K.J. Srearam and T. Ramasami, "*Sustaining Tanning Process Through Conservation, Recovery And Better Utilization Of Chromium*", J. Resources Conservation and Recycling, vol. 38, pp. 185-212, 2003.

[6] J. Ammenn, "*100 Years of Syntans How Chemistry Enabled İncreasing Performance On Leather*", XXXII. Congress of IULTCS, İstanbul-Turkey, 29-31 May, 2013.

[7] J. Ammenn, C. Huebsch, E. Schilling, B. Dannheim, "*Chemistry of Syntans And Their İnfluence On The Leather Quality*", Journal of The American Leather Chemists Association, Vol. 110 (11), pp. 349-354, 2015.

[8] E.N. Daniel, C. Stamford, "*Preparation of Sulfonated Phenolic Resins*", US Patent No: 2.621.164. 1952.

[9] Y. Dikmelik, "*Deri Teknolojisi*", İzmir: Sepici Kültür Hizmeti Yayınları, 2013.

[10] J., Miglarese, "*Manufacture of Syntans From Vanillin And Leather Tanned Therewith*", Us Patent No: 2.564.022, 1951.

[11] A. Stanley, L. Livingston, J.M. Kelly, N.J. Belford, "*Condensates of Sulfonated Formaldehyde-Mexed Phenols Condensates With Formaldehyde And A Phenol*", Us Patent No:3.442.859, 1969.

[12] E. Wolesensky, "Investigation of Synthetic Tanning Material, Technologic Papers of the Bureau of Standards", No.302, Government printing office, Washington. 1925.

[13] E. Wolesensky, "*Action of Sodium Sulphate In Synthetic Tanning Materials, Technologic Papers of the Bureau of Standards*", No.317, Government printing office, Washington, 1926a.

[14] E. Wolesensky, "*Analysis of Synthetic Tanning Materials, Technologic Papers of the Bureau of Standards*", No.316, Government printing office, Washington, 1926b.

[15] E. Wolesensky, "*Behavior of Synthetic Tanning Materials, Toward Hide Substance Technologic Papers of the Bureau of Standards*", No.309, Government printing office, Washington, 1926c.

[16] Y.Z. Wang, J.B. Li, Z.H. Shan, "*A novel synthesized melamine compound for leather making*", Journal of the American Leather Chemists Association, vol. 101, pp. 38-42, 2017.

[17] IUP 16, Leather Physical and Mechanical Tests, "Determination of Shrinkage Temperature up to 100 degrees", 2002.

[18] TS EN ISO 3376, Leather - Physical and Mechanical Tests - Determination of Tensile Strength and Percentage Extension, 2012.IUP 8, "Measurement of tear load – double edge tear", JSLTC, vol. 84, pp. 327-329, 2000.

[19] TS EN ISO 3377-2, Leather - Physical and Mechanical Tests - Determination of Tear Load Part 2: Double Edge Tear, 2016.